Mechanisms of Arsenic Uptake and Metabolism by Plants: Focusing on Rice

Guo-Xin Sun[1], Paul N. Williams[1], Yong-Guan Zhu[1, 2*]
[1]Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, [2]Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361003, China.
[*corresponding author: ygzhu@rcees.ac.cn]

Abstract: Rice, supporting 50% of world population, has high capacity of arsenic accumulation. In populations not exposed to As-tainted water, rice consumption is the largest contributor to the dietary As intake. Understanding the mechanisms of As uptake by rice and accumulation as well as speciation in grain is very important and urgent for health safety. Here we described As absorption from paddy soil, translocation from root to shoot, especially accumulation and speciation in rice grain.
Keywords: Arsenic, translocation, bran.

Introduction

Rice, the staple for around half of the world's population, can grow from ~50 degree north latitude to ~35 degree south latitude and from plain to plateau (an elevation of 2700 meters). It is grown widely in South and Southeast Asia. Compared with other cereals (wheat, barley, and maize), rice is much more efficient at accumulating arsenic (As) into its grain (1, 2), especially under the flooded conditions (3). All soils, including rice paddies, naturally contain As (4), which is class 1 carcinogen (10, 11). Soil As contamination has occurred in some areas through mining activities, irrigation with As-contaminated groundwater, and the use of arsenical compounds as herbicides, insecticides and wood preservatives. Rice is by far the largest food dietary source of As for populations beside drinking water with elevated As (12, 13). It is therefore important to investigate the As absorption and transformation from root to grain by rice.

Survey of arsenic in rice and rice products

Rice is particularly susceptible to As accumulation compared to other cereals. Baseline levels of As are about 10-fold higher than other cereal grains (14). Inorganic arsenic and dimethylarsinic (DMA) dominate grain arsenic speciation (15-19). It is believe that inorganic As representing between 20% and 90% of the total As in rice grain (5–8), is more toxic than methylated As compounds (6, 9). In Asian countries, the total As and percentage of inorganic As is relatively higher, especially for Bangladesh and India, indicating the content of highly toxic inorganic As in rice in these region is larger (20).

Brown, polished (or white) rice and rice bran are utilized in a very wide range of foods such as: crisped rice, puffed rice, rice crackers, cereal bars, rice flour, rice noodles, fermented condiments (miso and mirin), rice malt, rice wine, rice bran oil. Rice based products are marketed as healthy functional or "super" foods such as stabilized bran flour and bran solubles. Studies have shown that total arsenic levels were much higher in bran than in endosperm (white rice) obtained from the same whole grain rice (21-23). Rice bran solubles are popular rice bran product that has been heat treated to prolong shelf-life and then enzymatically extracted to collect water soluble components. We have found that commercially bought rice bran products from the US and Japan (excluding bran derived oils) directly intended for human consumption can contain up to 2 mg/kg of inorganic As. Untreated rice bran might contain levels approaching 1 mg/kg (23).

Table 1. Inorganic As in commercial rice bran products.

Rice product	Total As (mg/kg)	Inorg. As (mg/kg)	Inorg. As (%)
bran solubles	1.08 ± 0.02	0.71 ± 0.04	94.9
bran solubles	1.19 ± 0.03	0.86 ± 0.01	96.5
bran solubles	0.82 ± 0.01	0.61 ± 0.03	95.7
bran solubles	1.16 ± 0.02	0.825 ±0.005	95.7
defatted bran	1.60 ± 0.02	1.16 ± 0.05	97.1
riceo – ex	1.98 ± 0.04	1.88 ± 0.02	96.9
bran	1.89 ± 0.05	1.65 ± 0.10	96.5
bran	0.71 ± 0.01	0.48 ± 0.02	92.1
bran	1.07 ± 0.002	0.64 ± 0.03	81.5
rice flour	0.29 ± 0.01	0.11 ± 0.01	36.9

Soil to grain transfer of arsenic

The speciation of arsenic in the soil environment is dynamic. It can be biotically and abiotically inter-converted between the dominant solution phase inorganic species of arsenate and arsenite, the oxidized and reduced forms respectively (24). Both of them can be taken up by rice roots (25). Iron plaque is commonly formed on the surfaces of roots of aquatic plants including rice by releasing oxygen to their rhizosphere through aerenchyma, resulting in the oxidation of ferrous iron to ferric iron, and the precipitation iron oxide on the root surface (26). It was composed dominantly of ferrihydrite (63%), goethite (32%) and siderite (5%) (27), all of which Fe oxides have strong adsorptive capacity for arsenate. The presence of iron plaque can sequester As and form a buffer zone that alters the entry of As into plants (28). The presence of iron plaque can potentially alter the traditionally perceived phosphate (P)-arsenate competition. For example, As concentrations in shoots were significantly lower in –P plants than in +P plants, possible due to As sequestration in iron plaque which was induced by P deficiency.

Biochemical and biological processes taking place in the rhizosphere by various microbes might influence the speciation of As and its bioavailability to plants. Mycorrhizal fungi and other microorganisms in the rhizosphere benefit the rice plants. There are many reports about effects of mycorrhizal fungi on As acquisition by plant. The fungi could restrict As translocation from roots to shoots although the mechanism is not clear and requires further investigations (29, 30). Other bacteria, such as ammonia-oxidizing archaea (AOA), bacteria (AOB), iron reducing bacteria, sulfate reducing prokaryotes, are abundant in paddy soil (31-34). Some of them involve in iron reduction or oxidation in paddy soil, probably cause the transformation of As species, leading to As co-precipitation with, or adsorption to, Fe(III) minerals in the soil. All this resulted in reduced As uptake by rice (34).

Translocation of As from roots to shoot and grain

Arsenic has been demonstrated to have, generally, a low mobility with respect to translocation from roots to shoots in rice. The ratio of xylem sap As to external As was reported a range from 0.30-0.56 for inorganic As, which is still much higher than the ratio in barley ranged from 0.07-0.09 (35). Total As in straw is 20 time higher on average than that in whole grain according to 141 Chinese rice samples, ranging from 4 to 58 times (Table 2). Arsenite appears to be the main As species that is transported from the root cortical cells to the xylem vessels because in all of the plant species studied, arsenite is the predominant form of As in the xylem sap, accounting for

60–100% of the total As.

Table 2. The ratio of As in straw and bran with whole grain

	As in Straw / As in Whole grain	As in Bran / As in Whole grain
Number	141	215
Average	20.5	44.8%
Min	4.0	24.2%
Max	58.1	70.1%

It is generally believed that As concentrations decrease in the order of roots > stems and leaves > husks > grain (24, 36, 37). There is no clear pattern though for As in husk, bran and its endosperm. It was easily taken for granted that from root to endosperm As concentration should decrease from husk to endosperm. Our results showed that not all samples follow this pattern. Some rice samples, such as Bangladesh and Vietnamese rice have higher capacity to accumulate As in rice bran than their corresponding husks (Table 3). In all Chinese samples except for China 3, arsenic concentrations in husks were much higher than in bran, especially in high As rice (China 4) (Table 3). China 3 with relatively low As in grain, has higher As level in bran. It seemed that bran accumulated more As than husk when they grow with relatively low As in the soil. Other forty Chinese grain samples with low As in rice, (total As in polished rice less than 0.15 mg/kg), were collected to make further confirmation. As concentration in all bran are higher than their corresponding husk As, 2.2 times on average. The reason for higher As accumulation in bran is still unclear, probably this is related to different rice cultivar and As contamination level. Contaminated Chinese rice was investigated by Lombi through various techniques, such as high-pressure liquid chromatography (HPLC)-inductively coupled plasma mass spectrometry (ICP-MS), X-ray absorption near-edge spectroscopy (XANES) and particle induced X-ray emission (PIXE) (37). For that rice As level in husk is much higher than that in bran. This difference is probably related to the way contaminants are distributed within the different organs. The high concentration of As in the husk is probably derived from the xylematic transport of As. Arsenite was translocated from root to shoot (35), probably up to husk. By contrast, accumulation of As in the grain occurs primarily through the phloem.

Table 3. Total As concentration in different fractions of rice grain (mg/kg)

	China				Bangladesh				Vietnam
	1	2	3	4	1	2	3	4	
Husk	2.55	7.90	0.902	27.774	0.68	0.92	0.90	0.59	0.597
Bran	1.56	3.47	1.271	7.509	1.67	1.64	1.75	1.09	0.966
Whole grain	0.25	0.76	0.133	0.930	0.31	0.39	0.32	0.23	0.276
Endosperm	0.17	0.33	0.071	0.252	0.17	0.18	0.22	0.19	0.216

As accumulation and speciation in grain

Rice bran, 7-10% of whole grain weight, contain 24-70% total As in whole grain according to specially milled 215 rice samples. The average arsenic percentage in bran is 45% of whole grain (Table 2), indicating that As is more preferentially accumulated in the bran. In fact, arsenic is not evenly distributed in the bran, but accumulated in a small area on the surface of the grain (38, 39). The area of As accumulation was located to the position of the ovular vascular trace (38, 39). It is reported that nutrients are transported to the endosperm through ovular vascular trace (40). Probably As together with some other nutrients was transported into endosperm, but difficult to diffuse physiologically from the surface to inside or is accumulated preferentially in the protein-rich tissue (aleurone). As speciation in bran was confirmed that 95% of total arsenic in bran are inorganic As (23). Further investigation showed that dimethylarsinic acid (DMA) and arsenite were dominant As species. A large proportion of arsenite in bran is complexed by thiol ligands, i.e. the speciation of As in bran and endosperm was dominated by As(III)–thiol complexes. It might be possible to control sulfur (S) or thiol level in grain to decrease the As accumulation.

Conclusion

Arsenic is taken up by root, translocated from shoot up to husk, and accumulated in the grain, especially bran. Many factors affected As absorption, translocation and speciation in grain. To decrease the total As in rice, there are still lots of work to do.

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